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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> <b>DETERGENT COMPOSITIONS COMPRISING GLYCERYL ETHERS</b>  <b>(57) Abstract</b>  <p>A detergent composition comprises (a) one or more glyceryl ethers of a C<sub>12</sub>-C<sub>18</sub> alkyl or alkenyl primary or secondary alcohol, at least 50 mole percent of the glyceryl ether being diglyceryl ether and not more than 25 mole percent of the glyceryl being monoglyceryl ether, and (b) an anionic detergent surfactant. The compositions, which may be in granular or liquid form, may also contain other conventional ingredients, e.g. other detergent surfactants, detergent building compounds, enzymes and bleaches.</p>		

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DETERGENT COMPOSITIONS COMPRISING GLYCERYL ETHERSField of the invention

The present invention relates to detergent compositions, especially heavy duty compositions, that contain one or more glyceryl ethers as a nonionic deterative surfactant.

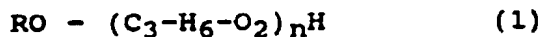
Background to the invention

Heavy duty detergents, whether in granular or liquid form, commonly comprise an anionic deterative surfactant, for example sodium (linear alkyl) benzene sulfonate in which the alkyl group preferably has 11-13 carbon atoms, or sodium alkyl sulfate, e.g that obtained by sulfating a C<sub>8</sub>-C<sub>18</sub> alkanol. To improve the performance of such detergent compositions against greasy stains and soils, it is conventional to include a nonionic deterative surfactant, typically a condensation product of a (C<sub>6</sub>-C<sub>15</sub> alkyl) phenol or a C<sub>8</sub>-C<sub>22</sub> alkanol with ethylene oxide. Preferred condensates are those containing 3-12 moles of ethylene oxide per mole of alkylphenol or 4-8 moles of ethylene oxide per mole of alkanol. A particular preferred nonionic is a condensate of C<sub>14</sub>-C<sub>15</sub> alkanol with 7 moles of ethylene oxide per mole of alkanol.

The ethylene oxide used in the preparation of the above discussed nonionics is, however, derived from oil and, furthermore, is a reagent that needs careful handling in order to minimise the risk of explosion. Thus, on account both of economics and of safety and other environmental considerations, it would be desirable to find an alternative nonionic surfactant.

Summary of the invention

The present invention relates to the use as a nonionic deterative surfactant in a detergent composition of one or more glyceryl ethers of the general formula



wherein

R represents an alkyl or alkenyl group of from 12 to 18 carbon atoms,  
 $C_3H_5O_2$  represents a divalent radical formed by removal from glycerol of an hydroxyl group and of the hydrogen from another hydroxyl group, and  
n is an integer,

in particular glyceryl ethers of which 50-100 mole percent is constituted by diglyceryl ether (  $n = 2$  ) and 0-25 mole percent is constituted by monoglyceryl ether (  $n = 1$  ), the remainder, if any, being constituted by triglyceryl ethers (  $n = 3$  ) and/or higher homologues ( $n > 3$ ).

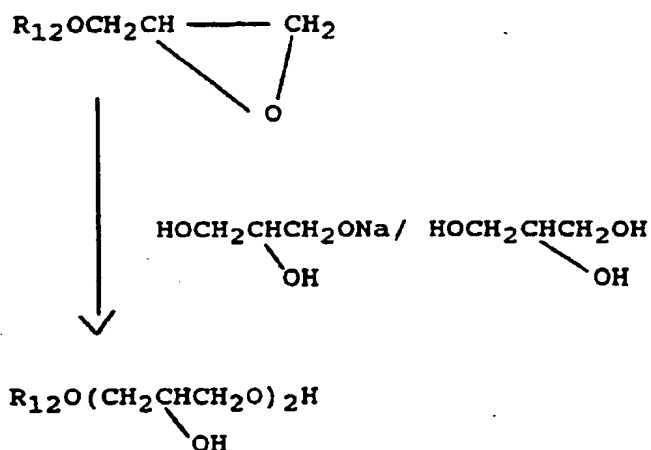
In one aspect, the present invention provides a detergent composition comprising (a) one or more glyceryl ethers of the general formula (1) as defined above and (b) an anionic deterative surfactant.

Description of exemplary embodiments.

The glyceryl ethers of the general formula (1) defined above are effective as nonionic deterative surfactants. At least 50 mole percent and preferably at least 60 mole percent of the glyceryl ethers of the formula (1) present in the detergent composition of this invention should be constituted by diglyceryl ether and not more than 25 mole percent, preferably not more than 20 mole percent should be constituted by monoglyceryl ether. The remainder, if any, of the glyceryl ether component (a) is constituted by triglyceryl ethers and/or higher homologues.

Generally, it has been found that the higher the content of diglyceryl ether in the glyceryl ether component (a), the better. It is preferred that diglyceryl ether should constitute 80 mole percent or more of the glyceryl ether component; it is particularly preferred that the glyceryl ether component of the present compositions should be substantially entirely composed of diglyceryl ether. Diglyceryl ethers may be prepared by a process known in principle from the article by H.Sagitani *et al*, entitled "Solution properties of homogenous polyglycerol dodecyl

ether nonionic surfactants", J.A.O.C.S., Vol. 66, No.1 (January 1989) pages 146-152. Specifically, Sagitani *et al* disclose the preparation of diglyceryl dodecyl ether by a process in which sodium is added to anhydrous glycerol under a nitrogen atmosphere, the solution is heated at 130°C for 1 hour, glycidyl dodecyl ether is added dropwise to the resultant sodium glycerate over 1 hour at 180°C, the mixture is stirred for 8 hours and the product is purified on a silica gel column using chloroform/methanol (98:2) as a solvent. Sagitani *et al* depicted the preparative process by means of the following reaction scheme:



wherein

$\text{R}_{12}$  represents the dodecyl radical.

The present applicant has found that the preparative process can be applied not just to the  $\text{R}_{12}$  compound but to compounds with any radical within the meaning specified for R in general formula (1) above. R is usually derived from a primary or secondary alcohol.

Furthermore, whereas the method taught by Sagitani *et al* depends upon a chromatographic purification, it has now been found that the principal by-product, glycerol cyclic dimer and also free fatty alcohol present in the epoxide can be removed to a satisfactory extent in a manner thought to be novel in this context, i.e. by simple distillation.

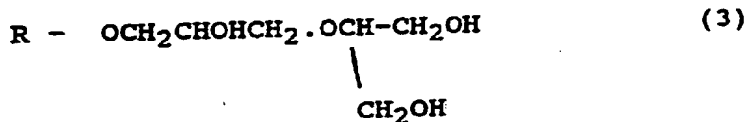
Thus it has been proved possible to obtain, using simple vacuum distillation, for example at a pot temperature of about 200°C, about 95% alkyl glyceryl ethers containing less than 2% cyclic by-product and less than 2% free fatty alcohol, without significant discoloration and degradation. This is surprising, particularly as Takaishi *et al* in US-A-4,465,866 (column 3, line 10-14) disparage distillation in processes for the preparation of polyol ethers as being irksome and incapable of industrial application.

Where the glyceryl ether product obtained by this process has less than the required molar percentage of diglyceryl ether and/or more than the specified maximum of monoglyceryl ether, the diglyceryl ether content can be worked up by conventional purification and isolation techniques.

It has also been found that, in addition to the diglyceryl ether of the formula



the diglyceryl ether of the formula



is also generally formed. Typically, about one mole of diglyceryl ether (3) is formed for every four moles of diglyceryl ether (2) that are produced.

Mixtures of or comprising the positional isomers of the formulae (2) and (3) are thought to be novel. Sagitani *et al*, *op.cit.*, disclose only the possibility of diastereomers, an aspect of optical isomerisms due to the fact that glycerol is prochiral. When preparing mixtures containing the isomer (3) it is thought that silica-gel chromatography should be avoided since the high *r* content of primary alcohol groups may be predicted to render the isomer more

substantive to silica gel and hence susceptible to removal. Mixtures of the position isomers (2) and (3) may well give rise to the better cleaning characteristics than the single isomer alone.

In general, the group R bonds to the first glycerol moiety at the primary site of the latter. The second glycerol could, in principle, bond to the secondary site of the first glycerol; in practice, however, it has generally been found that less than 10 mole percent of the diglyceride ethers have such bonding at the said secondary site.

R may represent a mixture of alkyl and/or alkenyl radicals, as will be the case, for example, when the glyceryl ethers are obtained from naturally occurring fatty alcohols ROH. An example is coconut alcohol, which contains primarily C<sub>12</sub>, C<sub>14</sub> and C<sub>16</sub> saturated alkyl radicals, with smaller amounts of C<sub>8</sub>, C<sub>10</sub> and C<sub>18</sub> alkenyl radicals. A preferred meaning for R is cocoyl, in particular so-called "topped and tailed" and "narrow-range" cocoyl, which is predominantly n-dodecyl (C<sub>12</sub>) and n-tetradecyl (C<sub>14</sub>).

The glycidyl alkyl (or alkenyl) ethers are known compounds, some of which may be obtained commercially, or may be prepared by methods known in principle. Thus, for example, a useful starting material is the alkyl glycidyl ether available under the trade name "Epoxide No. 8" from Proctor & Gamble, the alkyl groups in this epoxide being narrow-range cocoyl.

The diglyceryl ethers may also be prepared by a method known in principle from US-A-4,465,866 (Takaishi *et al*). This U.S. Patent teaches that a diglyceryl ether of the formula (2) given above can be prepared by reacting, in the presence of an acid or basic catalyst, an alkyl (or alkenyl) glycidyl ether with an acetal or ketal derivative of glycerol in order to obtain a 1, 3-dioxolane, which is then subjected to hydrolysis. Takaishi *et al* also mentions earlier proposals for the preparation of such diglyceryl ethers, in particular (i) the reaction of the linear dimer of glycerol with an alkali to form an alkali metal



alcoholate, which is then reacted with alkyl halide, and (ii) the reaction of an alcohol with a cyclic compound of the 1, 3-dioxolane type with hydrolysis of the resultant addition product (reference being made to Journal f. Prakt.Chemie, Band 316 (1974), 325-336).

The glyceryl ether components (a) will be present in the compositions of this invention in an amount usually of the form 0.5 to 30%, preferably from 3 to 15% and more preferably from 5 to 10 %, by weight.

The detergent compositions of this invention, which may be in liquid or granular form, will also contain at least one anionic deterative surfactant. Optionally, the composition may also comprise at least one other deterative surfactant, preferably selected from cationic, ampholytic and zwitterionic deterative surfactants, as well as other component conventional in the art, for example a builder, an enzyme, a bleach, a bleach activator, a polymeric soil-release agent, a chelating agent, a clay soil removal/anti-redeposition agent, a polymeric dispersing agent, a brightener, a suds suppressor, a pH-buffering agent, a dye or a pigment. It will be understood that any of the above mentioned components, whether essential or optional, may be constituted, if desired, by a mixture of two or more compounds of the appropriate description.

The deterative surfactant(s) will typically be used in a total amount of from 0 to 50, preferably 1 to 30 and more preferably 5 to 20 percent by weight.

Although the invention is especially useful in heavy duty or general purpose, laundry detergent compositions, the expression "detergent compositions" herein also includes dishwashing compositions, hard-surface and other household cleaners and personal care products such as shampoos.

Examples of anionic deterative surfactants and of the various optional components that come into consideration are as follows.

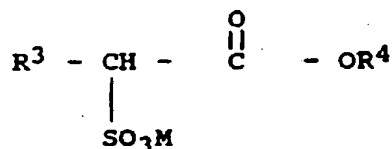
Anionic Surfactants

The detergent compositions of the present invention can contain, in addition to the nonionic surfactant system of the present invention, one or more anionic surfactants as described below.

Alkyl Ester Sulfonate Surfactant

Alkyl ester sulfonate surfactants hereof include linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sub>4</sub> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

Alkyl Sulfonate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl

having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g. an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Alkyl chains 12-16 carbon atoms, more preferably 14-15 carbon atoms are preferred.

#### Alkyl Alkoxyated Sulfate Surfactants

Alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO_3^M$  wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably an alkyl group having from 12 to 18 carbon atoms, especially from 12 to 15 carbon atoms.

A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

A preferred surfactant is C<sub>12</sub>-C<sub>15</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>15</sub>E(3.0)M). Other exemplary surfactants include C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(1.0)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>18</sub>E(2.25)M), C<sub>12</sub>-C<sub>18</sub> alkyl

polyethoxylate (3.0) sulfate ( $C_{12}-C_{18}E(3.0)M$ ), and  $C_{12}-C_{18}$  alkyl polyethoxylate (4.0) sulfate ( $C_{12}-C_{18}E(4.0)M$ ), wherein M is conveniently selected from sodium and potassium.

#### Other Anionic Surfactants

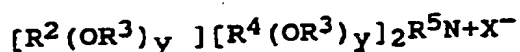
Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap,  $C_9-C_{20}$  linear alkylbenzenesulfonates,  $C_8-C_{22}$  primary or secondary alkanesulfonates,  $C_8-C_{24}$  olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British Patent specification No. 1,082,179,  $C_8-C_{24}$  alkylpolyglycethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated  $C_{12}-C_{18}$  monoesters) and diesters of sulfosuccinate (especially saturated and unsaturated  $C_6-C_{12}$  diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_kCH_2COO-M^+$  wherein R is a  $C_8-C_{22}$  alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface

Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Preferred anionic surfactants systems employed in the detergent compositions of the invention are free fo alkyl benzene sulfonate salts. A highly preferred system comprises a mixture of a major proportion of a C<sub>14</sub>-C<sub>15</sub> primary alkyl sulfate and a minor proportion of a C<sub>12</sub>-C<sub>15</sub> alkyl ethoxysulfate containing an average of three ethoxy groups per mole of alkyl ethoxy sulfate. The detergent compositions of the present invention typically comprise from about 1% to about 20 %, preferably from about 3% to about 15% and most preferably from 5% to 10% by weight of anionic surfactants.

#### Other Surfactants

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, and even further nonionic surfactants. Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammomium halogenides, and those surfactants having the formula:



wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-

$\text{CHOHCOR}^6\text{CHOHCH}_2\text{OH}$  wherein  $\text{R}^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when  $y$  is not 0;  $\text{R}^5$  is the same as  $\text{R}^4$  or is an alkyl chain wherein the total number of carbon atoms of  $\text{R}^2$  plus  $\text{R}^5$  is not more than about 18; each  $y$  is from 0 to about 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

Other cationic surfactants useful herein are also described in the U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 25%, preferably from about 3% to about 15% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin *et al.*, issued December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

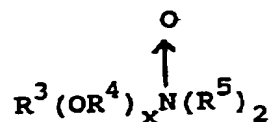
Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary

phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin *et al.*, issued December 30, 1975 at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein  $\text{R}^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $\text{R}^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $\text{R}^5$  is

an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $R^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure. These amine oxide surfactants in particular include  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

#### Nonionic surfactants

The detergent compositions of this invention may contain a nonionic surfactant in addition to the glyceryl ether component discussed above.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 8 carbon atoms, in either a straight-chain or branched-chain configuration, with from 1 to 12 moles of ethylene oxide per mole of alkyl phenol.

Suitable nonionics also include the condensation products of aliphatic alcohols containing from 8 to 22, preferably 12 to 18, carbon atoms, in either straight-chain or branched-chain configuration, with from 2 to 12, preferably 3 to 7, moles of ethylene oxide per mole of alcohol.

Suitable nonionic surfactants also include the fatty acyl or alkyl condensation products of carbohydrates and their derivatives such as glycosides, aminodeoxy forms, and polyols. Examples include coco-alkyl polyglucosides and tallow-acyl-N-methyl-glucamides.

The additional nonionic surfactants, if used, will generally be present at a level of up to 15 percent, usually from 1 to 6 percent, by weight of the composition.



### Builders

The detergent compositions of the present invention can comprise inorganic or organic detergent builders to assist in mineral hardness control.

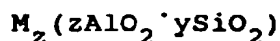
The level of builder can vary widely depending upon the end use of the composition and its desired physical form. Liquid formulations typically comprise at least about 1%, more typically from about 5% to about 50%, preferably from about 5% to about 30% by weight of the detergent builder. Granular formulations typically comprise at least about 1%, more typically from about 10% to about 80%, preferably from about 15% to about 50% by weight of the detergent builder. Lower or higher levles of builder, however, are not meant to be excluded.

Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C. Preferred builder systems are also free of phosphates.

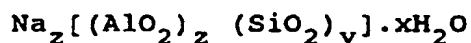
Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, incorporated herein by reference. However, other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bl aches, and as a comp nent of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesquicarbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, the disclosure of which is incorporated herein by reference.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



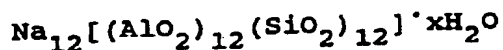
wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of  $CaCO_3$  hardness per gram of anhydrous aluminosilicate. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976, incorporated herein

by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



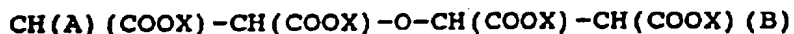
wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Specific examples of polyphosphates are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta phosphate in which the degree of polymerization ranges from about 6 to about 21, and salts of phytic acid. Examples of phosphonate builder salts are the water-soluble salts of ethane 1-hydroxy-1, 1-diphosphonate particularly the sodium and potassium salts, the water-soluble salts of methylene diphosphonic acid e.g. the trisodium and tripotassium salts and the water-soluble salts of substituted methylene diphosphonic acids, such as the trisodium and tripotassium ethylidene, isopropylidene benzylmethylidene and halo methylidene phosphonates. Phosphonate builder salts of the aforementioned types are disclosed in U.S. Patent Nos. 3,159,581 and 3,213,030 issued December 1, 1964 and October 19, 1965, to Diehl; U.S. Patent No. 3,422,021 issued January 14, 1969, to Roy; and U.S. Patent Nos. 3,400,148 and 3,422,137 issued September 3, 1968, and January 14, 1969 to Quimby, said disclosures being incorporated herein by reference. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the

form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium salts, especially sodium salts, or ammonium and substituted ammonium ( e.g., alkanolammonium ) salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti *et al.*, U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.

A specific type of ether polycarboxylates useful as builders in the present invention also include those having the general formula:

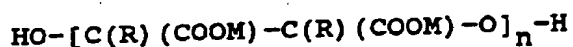


wherein A is H or OH; B is H or  $\text{-O-CH(COOX)-CH}_2\text{(COOX)}$ ; and X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydisuccinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is  $\text{-O-CH(COOX)-CH}_2\text{(COOX)}$ , then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly preferred are mixtures of TMS and TDS in a weight ratio of TMS to TDS of from about 97:3 to about 20:80. These builders are disclosed in U.S. Patent 4,663,071, issued to Bush *et al.*, on May 5, 1987.

Suitable ther polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those

described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

Other useful detergency builders include the ether hydroxypolycarboxylates represented by the structure:



wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R is the same or different and selected from hydrogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> substituted alkyl (preferably R is hydrogen).

Still other ether polycarboxylates include copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid.

Organic polycarboxylate builders also include the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids. Examples of polyacetic builder salts are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, and nitrilotriacetic acid.

Also included are polycarboxylates such as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, benzene pentacarboxylic acid, and carboxymethyloxysuccinic acid, and soluble salts thereof. Citric builders, e.g., citric acid and soluble salts thereof, is a polycarboxylate builders of particular importance for heavy duty liquid detergent formulations, but can also be used in granular compositions. Suitable salts include the metal salts such as sodium, lithium, and potassium salts, as well as ammonium and substituted ammonium salts.

Other carboxylate builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322, Diehl, issued March 28, 1973, incorporated herein by reference. Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Useful succinic acid builders include the  $C_5$ - $C_{20}$  alkyl succinic acids and salts thereof.

A particularly preferred compound of this type is dodecenylsuccinic acid. Alkyl succinic acids typically are of the general formula  $R-CH(COOH)CH_2(COOH)$  i.e., derivatives of succinic acid, wherein R is hydrocarbon, e.g.,  $C_{10}$ - $C_{20}$  alkyl or alkenyl, preferably  $C_{12}$ - $C_{16}$  or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Examples of useful builders also include sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclo-hexane-hexacarboxylate, cis-cyclopentane-tetracarboxylate, water-soluble polyacrylates (these polyacrylates having molecular weights to above about 2,000 can also be effectively utilized as dispersants), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene. Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226,

Crutchfield *et al*, issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Polycarboxylate builders are also disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other organic builders known in the art can also be used. For example, monocarboxylic acids, and soluble salts thereof, having long chain hydrocarbyls can be utilized. These would include materials generally referred to as "soaps." Chain lengths of  $C_{10}$ - $C_{20}$  are typically utilized.

The hydrocarbyls can be saturated or unsaturated.

#### Enzymes

Detersive enzymes can be included in the detergent compositions of the present invention for a variety of reasons including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active d tergents, builders and so on. In this respect bacterial or fungal enzymes are preferred,

such as bacterial amylases and proteases, and fungal cellulases.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name Esperase®. The preparation of this enzyme and analogous enzymes is described in British patent specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE™ and SAVINASE™ by Novo Industries A/S (Denmark) and MAXATASE™ by International Bio-Synthetics, Inc. (The Netherlands).

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A and methods for its preparation are described in European Patent Application 130,756, published January 9, 1985, incorporated herein by reference. Protease B is a proteolytic enzyme which differs from Protease A in that it has a leucine substituted for tyrosine in position 217 in its amino acid sequence. Protease B is described in European Patent Application Serial No. 87303761.8, filed April 28, 1987, incorporated herein by reference. Methods for preparation of Protease B are also disclosed in European Patent Application 130,756, Bott *et al.*, published January 9, 1985, incorporated herein by reference.

Amylases include, for example,  $\alpha$ -amylases obtained from a special strain of *B. licheniformis*, described in more detail in British patent specification No. 1,296,839 (Novo), previously incorporated herein by reference. Amylolytic proteins include, for example RAPIDASE™, International Bio-Synthetics, Inc. and TERMAMYL™, Novo Industries.



The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4, 435, 307, Barbesgaard *et al.*, issued March 6, 1984, incorporated herein by reference, which discloses fungal cellulase produced from *Hemicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Hemicola insolens* (*Hemicola grisea* var. *thermoidea*), particularly the *Hemicola* strain DSM 1800, and cellulases produced by a fungus of *Bacillus* N or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula* Solander).

Suitable lipase enzymes for detergent usage include those produced by micro-organisms of the of the *Pseudomonas* groups, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases of the present invention should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Ouchterlony (*Acta. Med. Scan.*, 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, *Th m et al.*, issued November 17, 1987, incorporated herein by r fer nce.

Typical examples thereof are the Amano-P lipase, the lipase ex Pseudomonas fragi FERM P 1339 (available under the trade name Amano-B), lipase ex Pseudomonas nitroreducens var. lipolyticum FERM P 1338 (available under the trade name Amano-CES), lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perbonate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application Wo 89/099813, published October 19, 1989, by O.Kirk, assigned to Novo Industries A/S, incorporated herein by reference.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. (incorporated herein by reference). Enzymes are further disclosed in U.S. Patent No. 4, 101, 457, Place et al., issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al., issued April 14, 1981, also incorporated herein by reference.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about

0.5 mg to about 3 mg, of active enzyme per gram of the composition.

For granular detergents, the enzymes are preferably coated or prilled with additives inert toward the enzymes to minimize dust formation and improve storage stability. Techniques for accomplishing this are well known in the art. In liquid formulations, an enzyme stabilisation system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate, and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. Patent 4,318,818, Letton *et al.*, issued March 9, 1982, incorporated herein by reference. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines ( e.g., alkanolamines such as diethanolamine, triethanolamine, di-isoropropanolamine, etc ), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn *et al.*, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, *et al.*, both incorporated herein by reference, and European Patent Application Publication No. 0 199 405, Application No.86200586.5, published October 29, 1986, Venegas. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,391, and 3,519,570.

#### Bleaching Compounds - Bleaching Agents and Bleaching

##### Activators

The detergent composition of the present invention may contain bleaching agents or bleaching compositions, containing bleaching agent or one or more bleach

activators. When included, present bleaching compounds will typically comprise from about 1% to about 20%, more typically from about 1% to about 10%, of such laundry detergent composition. In general, bleaching compounds are optional components in non-liquid formulations, e.g., granular detergents. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. For wash conditions below about 50°C, especially below about 40°C, it is preferred that the compositions hereof not contain borate or material which can form borate in situ (i.e. borate-forming material) under detergent storage or wash conditions. Thus it is preferred under these conditions that a non-borate, non-borate forming bleaching agent is used. Preferably, detergents to be used at these temperatures are substantially free of borate or borate-forming material. As used herein, "substantially free of borate or borate-forming material" shall mean that the composition contains not more than about 2% by weight of borate-containing and borate-forming material of any type, preferably, no more than 1%, more preferably 0%.

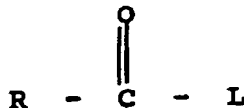
One category of bleaching agent which can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloroperbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns *et al.*, filed June 3, 1985, European Patent Application 0,133,354, Banks *et al.*, published February 20,

1985, and U.S. Patent 4,412,934, Chung *et al.*, issued November 1, 1983, all of which are incorporated by reference herein. Highly preferred bleaching agents also include 6-nonlamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns *et al.*, incorporated herein by reference.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide, and subject to the wash condition limitation previously mentioned, sodium perborate monohydrate and tetrahydrate.

Peroxygen bleaching agents are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator.

A wide range of bleach activators can be used, examples being disclosed in Spadini *et al.* USP 4179390. Preferred bleach activators include the tetraacetyl alkylene diamines, particularly tetraacetyl ethylene diamine (TAED) and tetraacetyl glycouril (TAGU).



wherein R is the alkyl group containing from about 1 to about 18 carbon atoms wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from about 6 to about 10 carbon atoms and L is a leaving group, the conjugate acid of which has a  $\text{pK}_a$  in the range from about 4 to 13. These bleach activators are described in U.S. Patent 4,915,854, issued April 10, 1990 to Mao *et al.*, incorporated herein by reference, and the U.S. Patent 4,412,934, which was previously incorporated herein by reference.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photo-activated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe *et al.*, incorporated herein by reference. Typically, detergent compositions will contain about 0.025% to about 1.25% by weight, of sulfonated zinc phthalocyanine.

#### Polymeric Soil Release Agent

Any polymeric soil release agents known to those skilled in the art can be employed in the detergent compositions of the present invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Polymeric soil release agents include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like.

Cellulosic derivatives that are functional as soil release agents are commercially available and include hydroxyethers of cellulose such as Methocel<sup>R</sup> (Dow).

Cellulosic soil release agents also include those selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl and C<sub>4</sub> hydroxyalkyl cellulose such as methylcellulose, ethylcellulose, hydroxypropyl methylcellulose, and hydroxybutyl methylcellulose. A variety of cellulose derivatives useful as soil release polymers are disclosed in U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, *et al.*, incorporated herein by reference.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g. C<sub>1</sub>-C<sub>6</sub> vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylen oxide backbones. Such materials are known in the art and are described in European Patent Application 0,219,048, published April 22, 1987 by Kud, *et al.* Suitable commercially available soil release agents of this kind include the Sokalan<sup>TM</sup> type of material, e.g., Sokalan<sup>TM</sup> HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. More specifically, these polymers are comprised of repeating units of ethylene terephthalate and PEO terephthalate in a mole ratio of ethylene terephthalate units to PEO terephthalate units of from about 25:75 to about 35:65, said PEO terephthalate units containing polyethylene oxide having molecular weights of from about 300 to about 2000. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976, which is incorporated by reference. See also U.S. Patent 3,893,929 to Basadur issued July 8, 1975 (incorporated by reference) which discloses similar copolymers.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene

terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000, and the mole ratio of ethylene terephthalate units to polyoxyethylene terephthalate units in the polymeric compound is between 2:1 and 6:1. Examples of this polymer include the commercially available material Zelcon<sup>R</sup> 5126 (from Dupont) and Milease<sup>R</sup> T (from ICI). These polymers and methods of their preparation are more fully described in U.S. Patent 4,702,857, issued October 27, 1987, to Gosselink, which is incorporated herein by reference.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyaleneoxy repeat units and terminal moieties covalently attached to the backbone, said soil release agent being derived from a allyl alcohol ethoxylate, dimethylterephthalate, and 1,2 propylene diol, wherein the terminal moieties of each oligomer have, on average, a total of from about 1 to about 4 sulfonate groups. These soil release agents are described fully in U.S. Patent 4,968,451, issued 6 November, 1990 to J. J. Scheibel and E. P. Gosselink, U.S. Serial No. 07/474,709, filed January 29, 1990, incorporated herein by reference.

Other suitable polymeric soil release agents include the ethyl- or methyl-capped 1,2-propylene terephthalate-polyoxy-ethylene terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987, to Gosselink et al., the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988, to Gosselink, wherein the anionic end-caps comprise sulfo-polyethoxy groups derived from polyethylene glycol (PEG), the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink, having polyethoxy end-caps of the formula  $X-(OCH_2CH_2)_n-$  wherein n is from 12 to about 43 and X is a C<sub>1</sub>-C<sub>4</sub> alkyl, or preferably



methyl, all of these patents being incorporated herein by reference.

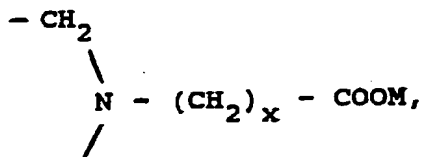
Additional soil release polymers include soil release polymers of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al., which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters, said patent being incorporated herein by reference. The terephthalate esters contain unsymmetrically substituted oxy-1,2-alkyleneoxy units.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, preferably from about 0.1% to about 5.0%, more preferably from about 0.2% to about 3.0% by weight of the laundry detergent compositions of the present invention.

#### Chelating Agents

The detergent compositions of the present invention may also contain one or more iron and manganese chelating agents as a builder adjunct material. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

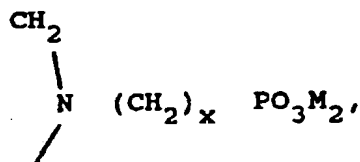
Amino carboxylates useful as optional chelating agents in compositions of the invention can have one or more, preferably at least two, units of the substructure



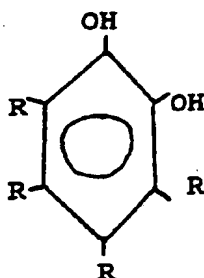
wherein M is hydrogen, alkali metal, ammonium or substituted ammonium (e.g. ethanolamine) and x is from 1 to about 3, preferably 1. Preferably, these amino

carboxylates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Operable amine carboxylates include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the detergent compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions. Compounds with one or more, preferably at least two, units of the substructure



wherein M is hydrogen, alkali metal, ammonium or substituted ammonium and x is from 1 to about 3, preferably 1, are useful and include ethylenediaminetetrakis (methylenephosphonates), nitrilotris (methylenephosphonates) and diethylenetriaminepentakis (methylenephosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Alkylene groups can be shared by substructures. Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. These materials can comprise compounds having the general formula:



wherein at least one R is  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  or soluble salts thereof and mixtures thereof. U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al., incorporated herein by reference, discloses polyfunctionally-substituted aromatic chelating and sequestering agents. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfo- benzene. Alkaline detergent compositions can contain these materials in the form of alkali metal, ammonium or substituted ammonium (e.g. mono-or triethanol-amine) salts.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the laundry detergent compositions of the present invention. More preferably chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Clay Soil Removal/Anti-redeposition Agents

Clay soil removal/anti-redeposition agents useful in the detergent compositions of the present invention include polyethylene glycols and water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Polyethylene glycol compounds useful in the detergent compositions of the present invention typically have a molecular weight in the range of from about 400 to about 100,000, preferably from about 1,00 to about 20,000, more preferably from about 2,000 to about 12,000, most preferably from about 4,000 to about 8,000. Such compounds are commercially available and are sold as Carbowax<sup>®</sup>,

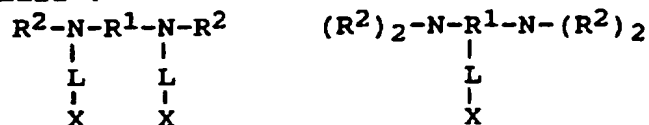
which is available from Union Carbide, located in Danbury, Conn.

The water soluble ethoxylated amines are preferably selected from the group consisting of :

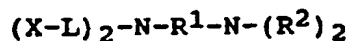
(1) ethoxylated monamines having the formula :



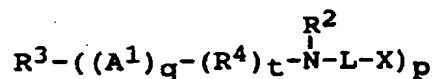
(2) ethoxylated diamines having the formula :



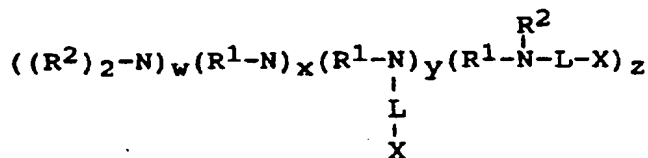
or



(3) ethoxylated polyamines having the formula :

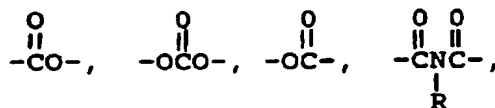
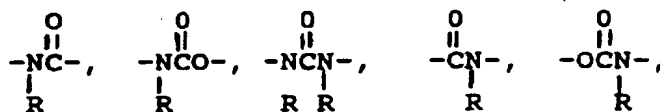


(4) ethoxylated amine polymers having the general formula :



and

(5) mixtures thereof; wherein  $A^1$  is :



or -O-; R is H or C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl R<sup>1</sup> is C<sub>2</sub>-C<sub>12</sub> alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R<sup>2</sup> is C<sub>1</sub>-C<sub>4</sub> or hydroxyalkyl, the moiety -L-X, or two R<sup>2</sup> together form the moiety -(CH<sub>2</sub>)<sub>r</sub>, -A<sup>2</sup>-(CH<sub>2</sub>)<sub>s</sub>-, wherein A<sup>2</sup> is -O- or -CH<sub>2</sub>-, r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; X is a nonionic group, an anionic group or mixture thereof; R<sup>3</sup> is a substituted C<sub>3</sub>-C<sub>12</sub> alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having substitution sites; R<sup>4</sup> is C<sub>1</sub>-C<sub>12</sub> alkylene, hydroxyakylene, alkenylene, arylene or alkarylene, or a C<sub>2</sub>-C<sub>3</sub> oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; L is a hydrophilic chain which contains the polyoxyalkylene moiety -((R<sup>5</sup>O)<sub>m</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>)-, wherein R<sup>5</sup> is C<sub>3</sub>-C<sub>4</sub> alkylene or hydroxyalkylene and m and n are numbers such that the moiety -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>- comprises at least about 50% by weight of said polyoxyalkylene moiety; for said monamines, m is from 0 to about 3, and n is at least about 6 when R<sup>1</sup> is C<sub>2</sub>-C<sub>3</sub> alkylene, hydroxyalkylene, or alkenylene, and at least about 3 when R<sup>1</sup> is other than C<sub>2</sub>-C<sub>3</sub> alkylene, hydroxyalkylene or alkenylene; for said polyamines and amine polymers, m is from 0 to about 10 and n is at least about 3; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z at least 2; and y + z is at least 2.

The most preferred soil release and anti-redeposition agent are ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986, incorporated herein by reference. Another group of preferred clay soil removal/anti-redeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984, incorporated herein by reference. Other clay soil

removal/anti-redeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985, all of which are incorporated herein by reference.

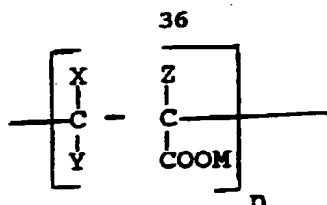
The most preferred soil release and anti-deposition agents are ethoxylated tetraethylenepentamine and the polyethylene glycols having a molecular weight in the range of from about 4,000 to about 8,000.

Granular detergent compositions which contain such compounds typically contain from about 0.01% to about 10.0% by weight of the clay removal agent; liquid detergent compositions typically contain from about 0.01% to about 5.0% by weight.

#### Polymeric Dispersing Agent

Polymeric polycarboxylate dispersing agents can advantageously be utilized in the detergent compositions of the present invention. These materials can aid in calcium and magnesium hardness control. In addition to acting as a builder adjunct analogously to the polycarboxylate described above in the Builder description, it is believed, though it is not intended to be limited by theory, that these higher molecular weight dispersing agents can further enhance overall detergent builder performance by inhibiting crystal growth of inorganics, by particulate soil peptization, and by antiredeposition, when used in combination with other builders including lower molecular weight polycarboxylates.

The polycarboxylate materials which can be employed as the polymeric polycarboxylate dispersing agent are these polymers or copolymers which contain at least about 60% by weight of segments with the general formula :



wherein X, Y, and Z are each selected from the group consisting of hydrogen, methyl, carboxy, carboxymethyl, hydroxy and hydroxymethyl; a salt forming cation and n is from about 30 to about 400. Preferably, X is hydrogen or hydroxy, Y is hydrogen or carboxy, Z is hydrogen and M is hydrogen, alkali metal, ammonia or substituted ammonium. Polymeric polycarboxylate materials of this type can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions have been disclosed, for example, in Diehl,

U.S. Patent No. 3,308,067, issued March 7, 1967. This patent is incorporated herein by reference.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing agent. Such materials include the water soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form ranges from about 5,000 to 100,000, preferably from about 6,000 to 60,000, more preferably from about 7,000 to 60,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, which publication is incorporated herein by reference.

If utilized, the polymeric dispersing agents will generally comprise from about 0.2% to about 10%, preferably from about 1% to about 5% by weight of the detergent compositions.

#### Brightener

Optical brighteners or other brightening or whitening agents known to those skilled in the art can be incorporated into the laundry detergent compositions of the present invention. However, the choice of brightener will depend upon a number of factors, such as the type of detergent, the nature of other components present in the detergent composition, the temperatures of wash wash, the degree of agitation, and the ratio of the material washed to tub size.

The brightener selection is also dependent upon the type of material to be cleaned, e.g. cottons, synthetics, etc. Since most laundry detergent products are used to clean a variety of fabrics, the detergent compositions should contain a mixture of brighteners which will be effective



for a variety of fabrics. It is of course necessary that the individual components of such a brightener mixture be compatible.

Commercial optical brighteners can be classified into subgroups which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982), the disclosure of which is incorporated herein by reference.

Stilbene derivatives include, but are not necessarily limited to, derivatives of stilbene; triazole derivatives of stilbene; oxadiazole derivatives of stilbene; oxazole derivatives of stilbene; and styryl of stilbene.

Certain derivatives of bis(triazinyl) aminostilbene may be prepared from 4,4'-diamine-stilbene-2,2'-disulfonic acid.

Coumarin derivatives include, but are not necessarily limited to, derivatives substituted in the 3-position, in the 7-position, and in the 3- and 7-positions.

Carboxylic acid derivatives include, but are not necessarily limited to, fumaric acid derivatives; benzoic acid derivatives; p-phenylene-bis-acrylic acid derivatives; naphthalenedicarboxylic acid derivatives; heterocyclic acid derivatives; and cinnamic acid derivatives.

Cinnamic acid derivatives can be further subclassified into groups which include, but are not necessarily limited to, cinnamic acid derivatives, styrylazoles, styrylbenzofurans, styryloxadiazoles, styryltriazoles, and styrylpolyphenyls, as disclosed on page 77 of the Zahradnik reference.

The styrylazoles can be further subclassified into styrylbenzoxazoles, styrylimidazoles and styrylthiazoles, as disclosed on page 78 of the Zahradnik reference. It will be understood that these three identified subclasses

may not necessarily reflect an exhaustive list of subgroups into which styrylazoles may be subclassified.

Other optical brighteners are the derivatives of dibenzothiophene-5,5-dioxide disclosed at page 741-749 of The Kirk-Othmer Encyclopedia of Chemical Technology, Volume 3, pages 737-750 (John Wiley & Son, Inc., 1962), the disclosure of which is incorporated herein by reference, and include 3,7-diaminodibenzothiophene-2, 8-disulfonic acid, 5, 5 dioxide.

Other optical brighteners are azoles, which are derivatives of 6-membered ring heterocycles. These can be further subcategorized into monoazoles and bisazoles. Examples of monoazoles and bisazoles are disclosed in the Kirk-Othmer reference. Still other optical brighteners are the derivatives of 6-membered-ring heterocycles disclosed in the Kirk-Othmer reference. Examples of such compounds include brighteners derived from pyrazine and brighteners derived from 4-aminonaphthalamide.

In addition to the brighteners already described, miscellaneous agents may also be useful as brighteners. Examples of such miscellaneous agents are disclosed at pages 93-95 of the Zahradnik reference, and include 1-hydroxy-3,6,8-pyrenetrisulfonic acid; 2,4-dimethoxy-1,3,5-triazin-6-yl-pyrene; 4,5-diphenylimidazolonedisulfonic acid; and derivatives of pyrazolinequinoline.

Other specific examples of optical brightener are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988, the disclosure of which is incorporated herein by reference. These brighteners include the Phorwhite<sup>TM</sup> series of brighteners from Verona. Others brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styrylphenyl)-2H-naphthol(1,2-d)triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilben; 4,4'-bis(styryl)bisphenyls; and the  $\gamma$ -aminocoumarins. Specific examples of these brighteners include

4-methyl-7-diethylamino coumarin; 1,2-bis(-bensimidazol-2-yl)-ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)-thiophene; 2-styryl-naphth-(1,2-d)-oxazole; and 2-(stilbene-4-yl)-2H-naphtho(1,2-d)triazole.

Still other optical brighteners include those disclosed in U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton, the disclosure of which is incorporated herein by reference.

If utilized, the optical brighteners will generally comprise from about 0.05% to about 2.0%, preferably from about 0.1% to about 1.0% by weight of the laundry detergent compositions.

#### Suds Suppressors

Compounds known, or which become known, for reducing or suppressing the formation of suds can be incorporated into the detergent compositions of the present invention. The incorporation of such materials, hereafter "suds supressor", can be desirable because the polyhydroxy fatty acid amide surfactants hereof can increase suds stability of the detergent compositions. Suds suppression can be of particular importance when the detergent compositions include a relatively high sudsing surfactant in combination with the polyhydroxy fatty acid amide surfactant. Suds suppression is particularly desirable for compositions intended for use in front loading automatic washing machines. These machines are typically characterized by having drums, for containing the laundry and wash water, which have a horizontal axis and rotary action about the axis. This type of agitation can result in high suds formation and, consequently, in reduced cleaning performance. The use of suds suppressors can also be of particular importance under hot water washing conditions and under high surfactant concentration conditions.

A wide variety of materials may be used as suds suppressors. Suds suppressors are well known to those skilled in the art. They are generally described, for example, in Kirk Othmer Encyclopedia of Chemical

Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acids and soluble salts thereof. These materials are discussed in U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John, said patent being incorporated herein by reference. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressors typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts. These materials are a preferred category of suds suppressor for detergent compositions.

The detergent compositions of the present invention may also contain non-surfactant suds suppressors. These include, for example, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g. stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylemlamines or di- to tetra-alkylaldimine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., sodium, potassium, lithium) phosphates and phosphate esters. The hydrocarbons, such as paraffin and haloparaffin, can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than about 100°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for

detergent compositions. Hydrocarbon suds suppressors are described for example in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al., incorporated herein by reference. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin", as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al., and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M.S., both incorporated herein by reference.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839, which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al., and in U.S. Patent 4,652,392, Baginski et al., issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of :

- (i) Polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1500 cs. at 25°C;

- (ii) From about 5 to about 50 parts per 100 parts by weight of :
  - (i) of siloxane resin composed of  $(\text{CH}_3)_3\text{SiO}_{1/2}$  units of  $\text{SiO}_2$  units in a ratio of from  $\text{CH}_3)_3\text{SiO}_{1/2}$  units and to  $\text{SiO}_2$  units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of :
  - (i) of a solid silica gel :

Suds suppressors, when utilized, are present in a "suds suppressing amount". By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will control the suds to the extent desired. The amount of suds control will vary with the detergent surfactant selected. For example, with high sudsing surfactants, relatively more of the suds controlling agent is used to achieve the desired suds control than with low foaming surfactants.

The detergent compositions of the present invention will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts thereof, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl

phosphates are generally utilized in amounts ranging from about 0.1% to about 2% by weight of the compositions. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used.

#### Other Ingredients

A wide variety of other ingredients which can be included in the detergent compositions of the present invention include other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulation.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, and polyols such as those containing from about 2 to about 6 carbon atoms and from about 2 to about 6 hydroxy groups ( e.g. propylene glycol, ethylene glycol, glycerine, and 1,3-propandiol ) can also be used.

The detergent composition of the present invention will preferably be formulated such that during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and 11, preferably between about 7.5 and about 10.5. Liquid product formulations preferably have a pH between about 7.5 and about 9.5, more preferably between about 7.5 and about 9.0. Techniques for controlling pH at recommended usage levels include the use of buffers, alkali, acids, etc., and are well known to those skilled in the art.

This invention further provides a method for cleaning substrates, such as fibres, fabrics, hard surfaces, skin, etc., by contacting said substrate with a detergent composition containing the glyceryl ether component (a) and the anionic detergent surfactant component (b), in the presence of a solvent such as water or a water-miscible solvent ( e.g. a primary or secondary alcohol ). Agitation

is preferably provided for enhancing cleaning. Suitable means for providing agitation include rubbing by hand, preferably with the aid of a brush, or other cleaning device, automatic laundry washing machine, automatic dish washer or the like.

Although, as indicated above, it is possible to include conventional polyethoxylate nonionic surfactants in the present compositions, it is currently preferred not to do so. In fact, it is an advantage of the glyceryl ethers employed as component (a) that they allow the replacement of polyethoxylate nonionic surfactants, thereby obviating the need to use ethylene oxide, whilst obtaining excellent cleaning characteristics. Thus, the glyceryl ethers of the formula (1) are very effective against greasy stains whilst showing no significant weaknesses against other, e.g. particulate, stains: furthermore, the glyceryl ethers are satisfactory with regard to redeposition of soils. Furthermore, the glyceryl ethers exhibit further advantages, for example the stabilization of enzyme in heavy duty detergent liquids. Also, the glyceryl ethers have comparatively low melting points and their use as agglomerating agents comes into consideration.

The present invention is illustrated in and by the following Examples.

#### Example 1

Cocoyl diglyceryl ether was prepared by a method analogous to that described by Sagitani *et al.*, J.O.A.C.S, Vol. 66, No.1 (January 1989) page 146, using the following reagents:

30g (0.124 mole) distilled dodecyl Epoxide No.8 ( from Proctor and Gamble)

0.14 (  $6.2 \times 10^{-3}$  mole ) sodium

57g ( 0.62 mole ) anhydrous glycerol

The sodium and glyceryl were reacted together at 130°C for one hour under nitrogen. The epoxide was added dropwise over one hour to the reaction mixture and 180°C, the mixture then being stirred at that temperature for 8 hours. The reaction mix was dissolved in ethanol and treated with



pellets of carbon dioxide in order to neutralize the sodium. The mix was freed of ethanol on a rotary evaporator and then distilled (1.75 mmHg (233 Pa); 140°C head temperature) to remove a fore-fraction of glycerol dimer (identified as such using gas-liquid chromatography).

The dodecyl diglyceryl ether as produced was a low-melting (44-46°C) solid comprising 92% diglyceryl ethers, 1.5% monoglyceryl ethers and 2% triglyceryl ethers.

The diglyceryl ether contained approximately 4 moles of the "linear" ether of the general formula (2) per mole of the "branched" ether of the general formula (3).

The above synthesis may also be carried using Epoxide No. 8 to which a small amount of sodium borohydride has been added, in order to obtain the end product of improved color.

#### Example 2

Cocoyl diglyceryl ether was prepared by the method of Takaishi *et al.*, US-A-4,465,866, using the following reagents:

74.5g (0.5625 mole) acetone glycerol ketal (available under the trade name "Solketal" from Aldrich Chemical Company)

3.2g (0.018 mole) tetramethyldiaminohexane

45g (0.18 mole) Epoxide No. 8 (from Proctor and Gamble)

The acetone glycerol ketal and tetramethyldiaminohexane were mixed together and heated to 100°C. The epoxide was added dropwise over a period of 30 minutes, keeping the temperature between 100 and 110°C. The resultant mixture was then heated at that temperature for 6 hours. The product was distilled (1mm Hg (133Pa) at 52°C head temperature) to remove the excess acetone glycerol ketal, and was vacuum distilled further (4.5 mmHg (600 Pa) at a head temperature of 230°C) to collect the product (di x lane intermediate).

34.8g (0.09 m l ) of the diox lane int rm diate in 75ml of than l wer add d to 4.6g (0.046 mole) concentrated

sulfuric acid in 100ml of water, and the resultant mixture was heated to reflux for 4 hours. The solution was then neutralized with 3.6g (0.09 mole) sodium hydroxide when cool. The product was extracted using diethyl ether, dried over sodium sulfate and then evaporated to dryness on a rotary evaporator to give a golden paste.

### Example 3

A series of heavy duty liquid detergent compositions, A-C, were prepared, these compositions having the surfactant components shown in the following Table, in which the amount of each component is shown in percent by weight of the composition.

Table 1

<u>Surfactant</u>	<u>A</u>	<u>B</u>	<u>C</u>
NaCnAS	12.9	12.9	12.9
Nat. NI E07	8.4	-	-
Nat. NI E05	-	8.4	-
CnDGE	-	-	8.4

In the above Table 1, the surfactants are identified as follows:

NaCnAS	= sodium coconut-alkyl sulfate
Nat. NI E07	= condensate of naturally occurring fatty alcohol with, per mole, 7 moles of ethylene oxide.
Nat. NI E05	= condensate of naturally occurring fatty alcohol with, per mole, 5 moles of ethylene oxide.
CnDGE	= coconut alkyl diglyceryl ether (prepared as Example 1 above).

The compositions were tested against a variety of stains, wherein soiled loads were washed in a miniwasher at 60°C using city water ( 5 moles total hardness ), at 1 percent usage. The soiled loads were prepared by staining cotton or polyester/cotton (PC) swatches in conventional manner.

The stain-removal performance was judged by an expert panel in a known manner, the results being recorded in panel score units (psu) on the Scheffe scale, taking the results obtained using composition A as the standard (0.0). The results are given in the following Table:

Table 2

<u>Stain Removal (Cotton/PC)</u>	<u>B</u>	<u>C</u>
Greasy:	+0.4/+0.7	+1.4/+1.0
Make-Up	+0.6/+0.5	+1.8/+0.9
Lipstick	+0.5/+1.2	+2.3/+1.7
Spaghetti	+0.2/+0.4	+0.5/+0.3
DMO	+0.7/+0.6	+1.0/+0.9
Bleachable	-0.2/+0.2	+1.1/+0.9
Enzymatic	-0.1/0.0	+0.3/0.0
Particulate	-0.1/-0.6	+0.2/+1.1

Notes: "enzymatic" refers to stains removable with protease.

DMO = dirty motor oil

As will be seen from Table 2, the composition C, which is according to the present invention, exhibited an excellent cleaning performance, especially against greasy stains and particulate stains.

Example 4

A reference composition was prepared in the form of a heavy duty detergent liquid containing 7.25 percent by weight of linear alkyl benzene sulfonate, 1.75 percent coconut-alkyl sulfate, 9 percent of citric builder, 5 percent of other builder and 10 percent of condensate of fatty alkyl alcohol with, per mole, 7 moles of ethylene oxide.

A test composition was then prepared, this being essentially similar to the reference composition but with only 6 percent of the said fatty alkyl alcohol/ethylene oxide condensate but with 4 percent of coconut alkyl diglyceryl ether (prepared as in Example 1 above).

The compositions were tested against a variety of stains, the test method and the evaluation method being as described in Example 3. The results in psu for the test composition, relative to the reference compositions results as 0.0 for the stained cotton loads and the stained polyester/cotton loads, are given in the following Table.

Table 3

<u>Stain</u>	<u>Cotton</u>	<u>Polyester/Cotton</u>
Greasy	+0.7	+0.8
Bleachable	-0.1	-0.1
Enzymatic	-0.2	+0.1
Particulate	+0.3	-0.3
BMI empa	+0.1	+0.1

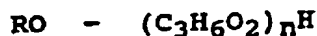
Note: BMI empa is a standardized soil comprised of blood, milk and ink on a polyester-cotton substrate and sold by EMPA Institute, St. Gallen, Switzerland.

Relative to the reference composition ( which typifies conventional heavy duty detergent liquid formulations), the test composition, which was formulated according to the present invention, showed improved performance against greasy stains with comparable performance against other stains.

It will of course be understood that the present invention has been described above purely by way of example and that modifications of detail can be made within the scope of the invention.

CLAIMS

1. A detergent composition comprising (a) one or more glyceryl ethers of the general formula :



wherein

R represents an alkyl or alkenyl group from 12 to 18 carbon atoms,

$C_3H_5O_2$  represents a divalent radical formed by removal from glycerol of a hydroxyl group and of the hydrogen atom from the remaining hydroxyl group, and

n is an integer,

at least 50 mole percent of component (a) being constituted by diglyceryl ether and not more than 25 mole percent of component -

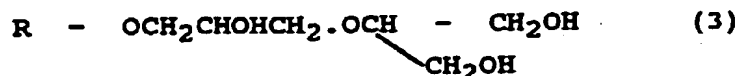
- (a) being constituted of monoglyceryl ether, and
- (b) an anionic deterative surfactant.

2. A composition according to claim 1., wherein at least 60 mole percent of component (a) is constituted by diglyceryl ether and not more than 20 mole percent of component (a) being constituted by monoglyceryl ether.

3. A composition according to claim 1. or 2. in which the diglyceryl ether of component (1) is a mixture comprising the diglyceryl ethers of the general formulae:



and



4. A composition according to the claim 3., in which the ethers of the formulae (2) and (3) are present in a molar ratio of about 4:1.

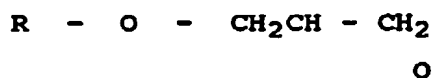
5. A composition according to any of the claims 1. to 4., in which component (a) is substantially entirely diglyceryl ether.

6. A composition according to any of the claims 1. to 5. in which R is a coconut alkyl group.

7. A composition according to any of the claims 1. to 6., which also comprises at least one further component selected from cationic, ampholytic, zwitterionic, and semi-polar deterative surfactants, detergency building agents, enzymes, bleaches and chelating agents.

8. A composition according to any of the claims 1. to 7. in the form of a heavy duty detergent liquid or a heavy duty detergent granule.

9. A process for the preparation of a diglyceryl ether of the formula (1) given in a claim 1, or a mixture of such ethers, wherein a compound of the general formula :



wherein R has the meaning given in claim (1), is reacted with glycerol in the presence of a base and/or with a glycerate and impurities in the product are removed by distillation.

10. The use, as above, as a deterative surfactant, of the diglyceryl ether of the formula (1) in claim 1., or a mixture of such ethers.

## INTERNATIONAL SEARCH REPORT

PCT/US92/09386

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :C11D 1/83, 1/66, 3/386

US CL :252/174.21, 174.22, DIG. 1, 549; 568/618, 680

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<input checked="" type="checkbox"/> X Y	US, A, 4,430,237 (Pierce et al) 07 February 1984, See column 3, lines 1-15 and column 5, lines 7-25.	<u>1-4</u> 1-4,9-10
A	US, A, 4,788,345 (Sebag et al) 29 November 1988, See column 1, lines 40-50.	
Y	US, A, 4,465,866 (Takaishi et al) 14 August 1984, See column 1, line 15 and column 5, lines 1-65.	1-4,9-10
Y	US, A, 4,298,764 (Berkowitz) 03 November 1981, See column 2, lines 45-68.	1-4,9-10
A	US, A, 3,879,475 (Wojtowicz et al) 22 April 1975, See column 1, lines 35-45.	

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be part of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* A	document member of the same patent family

Date of the actual completion of the international search 08 JANUARY 1999	Date of mailing of the international search report 26 JAN 1993
Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer KERY A. FRIES Telephone No. (703) 308-0687 INTERNATIONAL DIVISION

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/09386

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-8  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/09386

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,719,636 (Wojtowicz et al) 06 March 1973, See column 1, lines 35-45.	
Y	US, A, 4,206,070 (Jones) 03 June 1980, See column 2, lines 12-21 and column 4, lines 23-50.	1-4
A	US, A, (Kalopissis et al) 30 May 1972, See column 1, lines 45-50.	
A	Hayashi and Ochiai, "Solution Properties of Homogeneous Polyglycerol Dodecyl Ether Nonionic Surfactants," JAOCS vol. 66, no. 1 (January 1989).	

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/09386

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

Diglyceryl ether

monoglyceryl ether

anionic

252/clas